

**UNCLASSIFIED**

---

**AD 274 090**

*Reproduced  
by the*

**ARMED SERVICES TECHNICAL INFORMATION AGENCY  
ARLINGTON HALL STATION  
ARLINGTON 12, VIRGINIA**



---

**UNCLASSIFIED**

NOTICE: When government or other drawings, specifications or other data are used for any purpose other than in connection with a definitely related government procurement operation, the U. S. Government thereby incurs no responsibility, nor any obligation whatsoever; and the fact that the Government may have formulated, furnished, or in any way supplied the said drawings, specifications, or other data is not to be regarded by implication or otherwise as in any manner licensing the holder or any other person or corporation, or conveying any rights or permission to manufacture, use or sell any patented invention that may in any way be related thereto.

62-3-1

D1-82-0085

274090

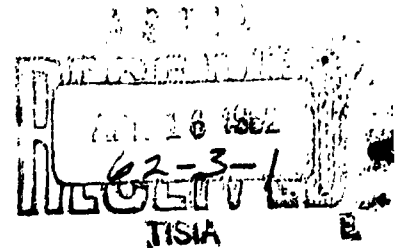
274 090

ASTIA

AD NO.

BOEING SCIENTIFIC  
RESEARCH  
LABORATORIES

The Electronic Structure of Decaborane-14



Emmett B. Moore, Jr.

Solid State Physics Laboratory

127450

February, 1962

D1-32-0085

THE ELECTRONIC STRUCTURE OF DECABORANE-14

by

Emmett B. Moore, Jr.

February, 1962

Boeing Scientific Research Laboratories  
Seattle, Washington

## Abstract

A linear combination of atomic orbitals treatment of the 22 framework atomic orbitals and 16 framework electrons of decaborane- $14$  yields eight bonding molecular orbitals with energies between  $-14.0$  ev and  $-11.1$  ev. An electron population analysis yields a charge of  $+0.41e$  on boron atoms 6 and 9,  $+0.01e$  on 5,7,8, and 10,  $-0.10e$  on 1 and 3, and  $-0.33e$  on 2 and 4. This charge distribution agrees satisfactorily with the charge distribution inferred from the reactions of decaborane- $14$  and gives a dipole moment of 7.3 D. If  $-0.2e$  is assigned to each bridge hydrogen, the dipole moment becomes 3.8 D, compared with the experimental value of 3.5 D. The polarizations of the first two allowed electronic transitions agree with the observed polarization, and the energy of the highest filled molecular orbital agrees satisfactorily with the observed ionization energy.

## I Introduction

The molecular structures of  $B_2H_6$ ,  $B_4H_{10}$ ,  $B_5H_9$ ,  $B_5H_{11}$ ,  $B_6H_{10}$ ,  $B_9H_{15}$  and  $B_{10}H_{14}$  are well known<sup>1</sup>, having been determined by means of X-ray or electron diffraction. Each of these compounds is characterized by the presence of bridge hydrogen atoms and by an overall deficiency of electrons. The bridge hydrogens are located, symmetrically or unsymmetrically, in the immediate vicinity of two boron atoms, and are presumably bound in some fashion to each. In the case of  $B_2H_6$  theory<sup>2</sup> and experiment<sup>3</sup> indicate that the bridge hydrogens are slightly negatively charged. The electron deficiency arises because there are more atomic orbitals than electrons available for bonding since each boron atom contributes four atomic orbitals but only three electrons. Also each boron atom is surrounded by as many as six nearest neighbors so there are too few electrons to form two electron localized bonds between all pairs of nearest neighbors. The boron hydrides thus are small molecules on the borderline between metals and non-metals and must be treated theoretically by some quantum mechanical treatment emphasizing delocalization of electrons, i.e., bonds in which the electrons are spread over more than two atoms. One such treatment has been carried out by Eberhardt, Crawford and Lipscomb<sup>4</sup> using three-center bonds. In this approximation three atomic orbitals, centered on three different atoms, and two electrons form a bond. This treatment accounts nicely for all the electrons and atomic orbitals available for bonding but does not in all cases yield very good dipole moments and charge distributions. In  $B_{10}H_{14}$ , for instance, the three-center bond charge distribution predicts atoms 5, 7, 8 and 10 to be the most positive whereas experiment indicates that atoms 6 and 9 are the most positive<sup>20</sup>

Also in  $B_{10}H_{14}$  the three-center bond treatment yields a dipole moment of 6.1 Debyes whereas the experimental dipole moment<sup>5</sup> is 3.52 D. The value 6.1 D has been recalculated from the parameters of Moore, Dickerson and Lipscomb<sup>6</sup>.

For  $B_2H_6$  a more complete self consistent field linear combination of atomic orbitals molecular orbital (SCF-LCAO-MO) treatment has been carried out by Hamilton<sup>2</sup>, yielding a charge distribution in closer agreement with experiment than the three-center bond treatment. Here, diborane was treated as a four-center, four-electron problem.

With this in mind, a modified LCAO-MO treatment has now been carried out for  $B_{10}H_{14}$  in the hope that it would yield a charge distribution and dipole moment in closer agreement with experiment than the three-center bond treatment and also in the hope that it would yield a better understanding of the general properties of delocalized bonds in boron hydrides.

## II Molecular Geometry

The decaborane molecule is shown in Figure 1. The boron atoms are numbered conventionally and the hydrogen atoms are numbered to correspond to the boron atoms. The lines connecting atoms merely join neighbors and are not to be construed as representing bonds. Figure 2 shows the ten borons and four bridge hydrogens projected onto the plane perpendicular to the two-fold axis. The molecule has been distorted in projection for clarity.

Atomic coordinates were taken from Moore, Dickerson and Lipscomb<sup>6</sup> and were transformed to fit the molecule with origin at the midpoint of  $B_1-B_3$ , x axis along  $O-B_3$ , z axis upward along the two-fold axis and y axis perpendicular to the x and z axes in the usual right-handed fashion. The new coordinates are listed in Table 1. Table 2 is a list of inter-atomic distances and angles derived from these coordinates.



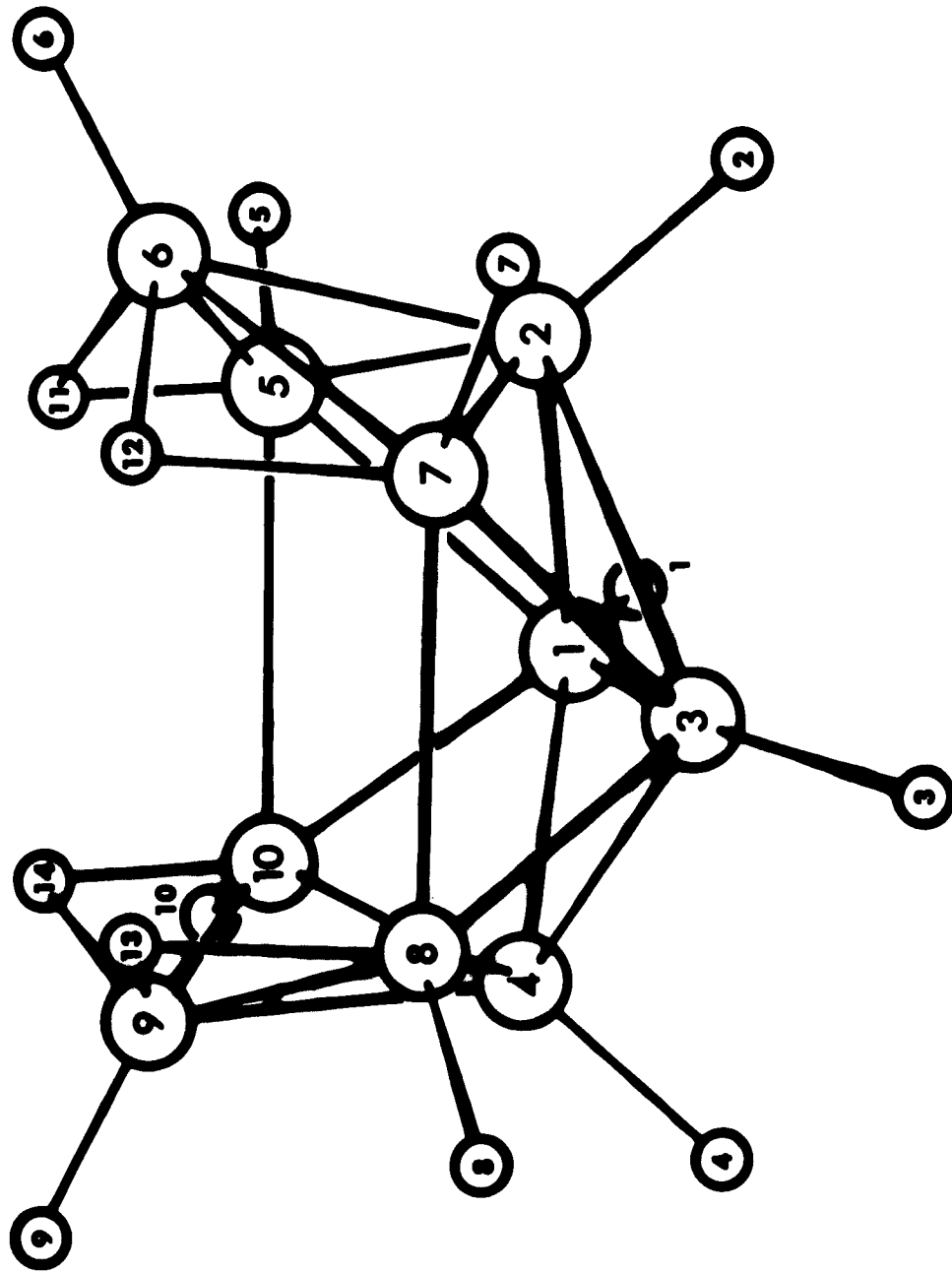
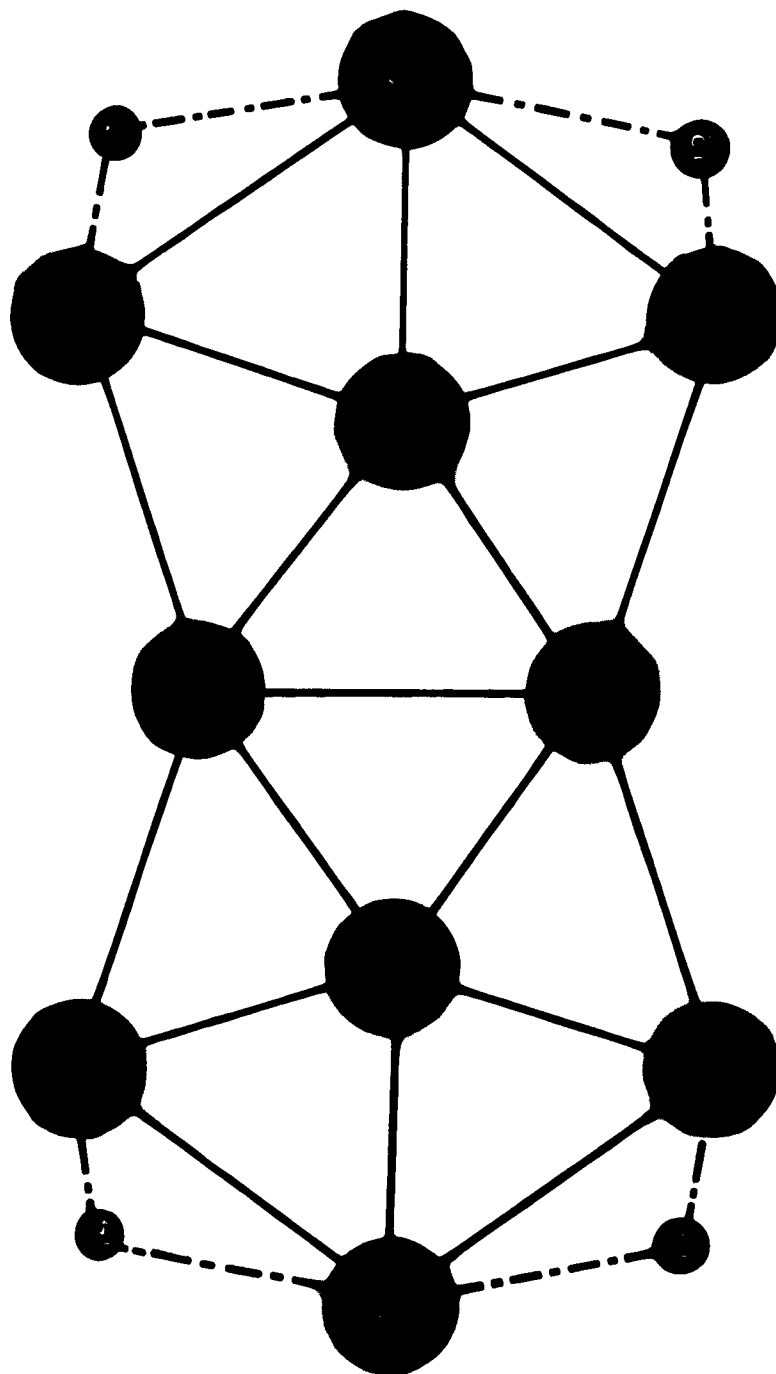


Figure 1.  $B_{10} H_{14}$



**Figure 2. B<sub>10</sub>H<sub>14</sub>**

|                 | x         | y        | z        | a               | b               |
|-----------------|-----------|----------|----------|-----------------|-----------------|
| B <sub>1</sub>  | -0.8548 Å | 0.0000 Å | 0.0000 Å | B <sub>1</sub>  | B <sub>3</sub>  |
| B <sub>2</sub>  | 0.0178    | 1.5226   | 0.4033   | B <sub>2</sub>  | B <sub>4</sub>  |
| B <sub>5</sub>  | -1.3812   | 1.0303   | 1.3575   | B <sub>5</sub>  | B <sub>8</sub>  |
| B <sub>6</sub>  | 0.0469    | 1.7746   | 2.1016   | B <sub>6</sub>  | B <sub>9</sub>  |
| B <sub>7</sub>  | 1.4417    | 0.9763   | 1.3575   | B <sub>7</sub>  | B <sub>10</sub> |
|                 |           |          |          |                 | $x_b = -x_a$    |
| H <sub>1</sub>  | -1.6480   | 0.0561   | -0.8463  | H <sub>1</sub>  | H <sub>3</sub>  |
| H <sub>2</sub>  | -0.2039   | 2.4226   | -0.4601  | H <sub>2</sub>  | H <sub>4</sub>  |
| H <sub>5</sub>  | -2.4712   | 1.8350   | 1.3575   | H <sub>5</sub>  | H <sub>8</sub>  |
| H <sub>6</sub>  | -0.0220   | 2.9511   | 2.6071   | H <sub>6</sub>  | H <sub>9</sub>  |
| H <sub>7</sub>  | 2.5645    | 1.4411   | 1.3575   | H <sub>7</sub>  | H <sub>10</sub> |
| H <sub>11</sub> | -1.1097   | 0.9350   | 2.5730   | H <sub>11</sub> | H <sub>13</sub> |
| H <sub>12</sub> | 1.1569    | 1.1129   | 2.7150   | H <sub>12</sub> | H <sub>14</sub> |
|                 |           |          |          |                 | $y_b = -y_a$    |
|                 |           |          |          |                 | $z_b = z_a$     |

Table 1. Atomic Coordinates. The coordinates of atoms in column b are related to those in column a by the two-fold rotation about z.

|  |  |  |
|--|--|--|
| B <sub>1</sub> -B <sub>2</sub> = 1.801 Å | B <sub>6</sub> -B <sub>7</sub> = 1.771 Å | B <sub>2</sub> -H <sub>1</sub> = 2.613 Å |
| B <sub>1</sub> -B <sub>3</sub> 1.710     | B <sub>6</sub> -B <sub>8</sub> 3.194     | B <sub>2</sub> -H <sub>2</sub> 1.267     |
| B <sub>1</sub> -B <sub>5</sub> 1.784     | B <sub>6</sub> -B <sub>9</sub> 3.550     | B <sub>2</sub> -H <sub>3</sub> 2.524     |
| B <sub>1</sub> -B <sub>6</sub> 2.895     | B <sub>7</sub> -B <sub>3</sub> 1.772     | B <sub>2</sub> -H <sub>5</sub> 2.684     |
| B <sub>1</sub> -B <sub>7</sub> 2.841     | B <sub>7</sub> -B <sub>4</sub> 3.047     | B <sub>2</sub> -H <sub>6</sub> 2.627     |
| B <sub>2</sub> -O 1.575                  | B <sub>7</sub> -B <sub>8</sub> 2.007     | B <sub>2</sub> -H <sub>7</sub> 2.721     |
| B <sub>2</sub> -B <sub>3</sub> 1.784     | B <sub>7</sub> -B <sub>9</sub> 3.215     | B <sub>2</sub> -H <sub>11</sub> 2.515    |
| B <sub>2</sub> -B <sub>4</sub> 3.045     | B <sub>7</sub> -B <sub>10</sub> 3.482    | B <sub>2</sub> -H <sub>12</sub> 2.610    |
| B <sub>2</sub> -B <sub>5</sub> 1.764     |  | B <sub>5</sub> -H <sub>5</sub> 1.355     |
| B <sub>2</sub> -B <sub>6</sub> 1.717     | B <sub>1</sub> -H <sub>1</sub> 1.161     | B <sub>5</sub> -H <sub>11</sub> 1.249    |
| B <sub>2</sub> -B <sub>7</sub> 1.799     | B <sub>1</sub> -H <sub>3</sub> 2.643     | B <sub>6</sub> -H <sub>2</sub> 2.654     |
| B <sub>2</sub> -B <sub>8</sub> 3.047     | B <sub>1</sub> -H <sub>5</sub> 2.797     | B <sub>6</sub> -H <sub>6</sub> 1.282     |
| B <sub>2</sub> -B <sub>9</sub> 3.709     | B <sub>1</sub> -H <sub>10</sub> 2.616    | B <sub>6</sub> -H <sub>11</sub> 1.505    |
| B <sub>5</sub> -B <sub>3</sub> 2.811     | B <sub>1</sub> -H <sub>11</sub> 2.750    | B <sub>6</sub> -H <sub>12</sub> 1.432    |
| B <sub>5</sub> -B <sub>6</sub> 1.774     | B <sub>1</sub> -H <sub>14</sub> 2.950    | B <sub>7</sub> -H <sub>7</sub> 1.215     |
| B <sub>5</sub> -B <sub>7</sub> 2.823     |  | B <sub>7</sub> -H <sub>12</sub> 1.394    |
| B <sub>5</sub> -B <sub>8</sub> 3.446     |  |  |
| B <sub>6</sub> -O 2.751                  |  | H <sub>2</sub> -O 2.474                  |
| B <sub>6</sub> -B <sub>3</sub> 2.867     |  | H <sub>5</sub> -H <sub>11</sub> 2.035    |
|  |  | H <sub>6</sub> -H <sub>11</sub> 2.291    |
|  |  | H <sub>6</sub> -H <sub>12</sub> 2.186    |
|  |  | H <sub>7</sub> -H <sub>12</sub> 1.983    |
|  |  | H <sub>11</sub> -H <sub>12</sub> 2.278   |

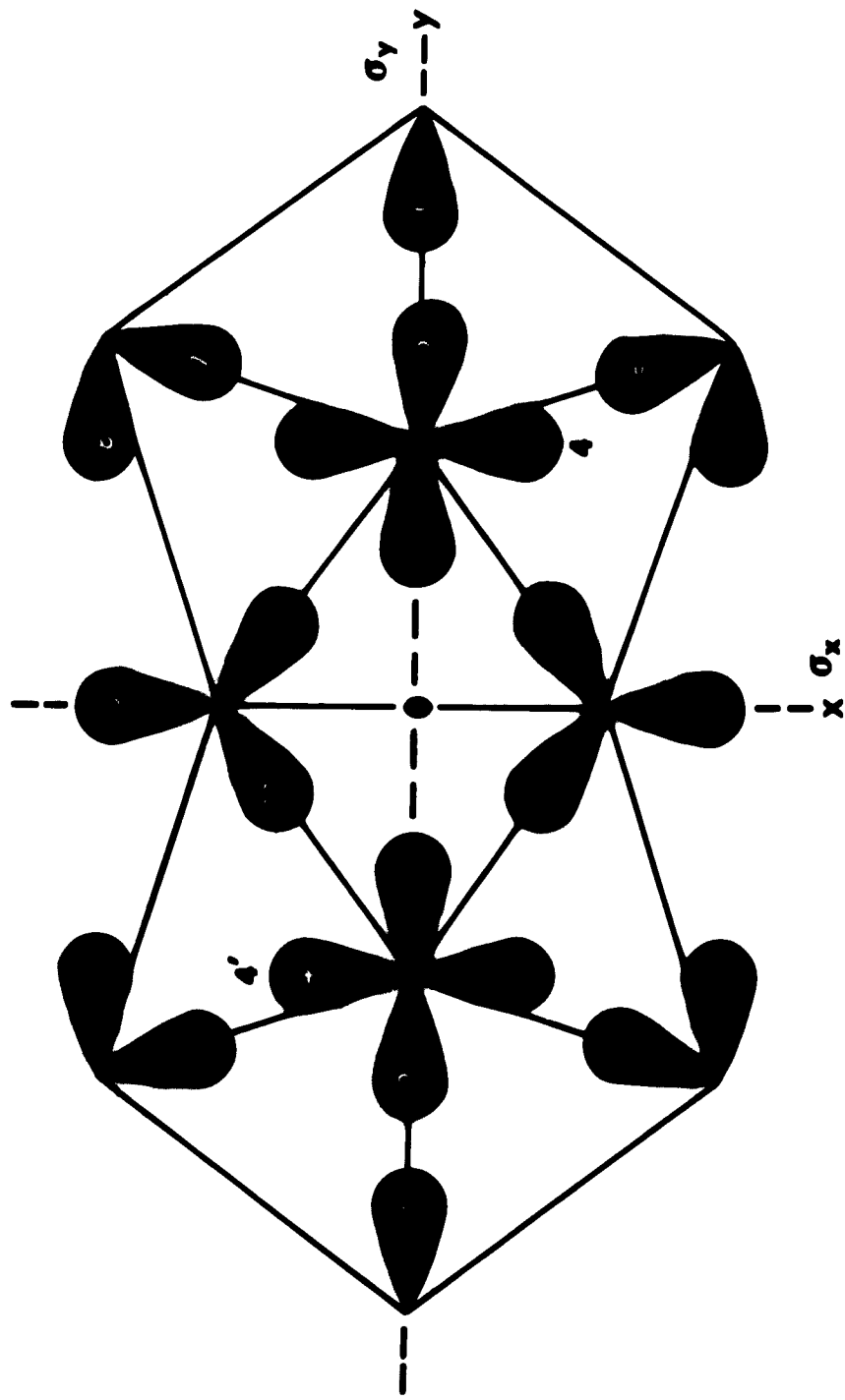
Table 2. Interatomic Distances

### III Atomic Orbitals

To form the molecular orbitals it is necessary to select suitable atomic orbitals. Here it was assumed that each hydrogen atom contributes one 1s AO and one electron and that each boron atom contributes one 2s, one  $2p_x$ , one  $2p_y$  and one  $2p_z$  AO and 3 electrons, a total of 54 AO's and 44 electrons for the molecule. The AO's located on each boron were hybridized as suggested by the structure to form tetrahedral hybrids on atoms 1, 3, 5, 6, 7, 8, 9 and 10 and trigonal hybrids on atoms 2 and 4. One hybrid orbital from each boron points directly toward its terminal hydrogen. Two hybrids from each of boron atoms 6 and 9 point toward bridge hydrogens and one hybrid from each of atoms 5, 7, 8 and 10 points toward the nearest bridge hydrogen. The terminal hydrogens were assumed to be bonded to the corresponding boron atoms by two-center, two-electron, non-polar bonds and the bridge hydrogens were each assumed to be bonded to the two neighboring borons by three-center, two-electron bonds. This uses 32 atomic orbitals and 28 electrons. The remaining 16 electrons must then be fitted into MO's which are linear combinations of the 22 remaining hybrid orbitals. These hybrids are all boron (framework) orbitals and are shown in projection in Figure 3. Orbital 1 is a tetrahedral hybrid ( $sp^3$ ) located on boron 6 pointing toward boron 2. Orbital 2 is a trigonal hybrid ( $sp^2$ ) located on boron 2 pointing toward boron 6. Orbital 3 is an  $sp^2$  hybrid on boron 2 pointing toward the origin. Orbital 4 is a pure p orbital on boron 2 with its positive direction in the direction of the x axis. Orbital 5 is an  $sp^3$  hybrid on boron 7 pointing toward boron 2. Orbital 6 is an  $sp^3$  hybrid on boron 7 pointing toward the midpoint of the triangle formed by borons 3, 7 and 8. Orbital 7 is an  $sp^3$  hybrid on boron 5 pointing toward boron 2. Orbital 8 is an  $sp^3$  hybrid on boron 5 pointing

toward the midpoint of the triangle formed by borons 1, 5 and 10. Orbital 9 is an  $sp^3$  hybrid on boron 1 pointing toward the midpoint of the triangle formed by borons 1, 5 and 10. Orbital 10 is an  $sp^3$  hybrid on boron 1 pointing toward the projection of boron 2 on the x-y plane. Orbital 11 is an  $sp^3$  hybrid located on boron 1 pointing toward the projection of boron 4 on the x-y plane. Hybrids 10 and 11 lie in the x-y plane. The primed hybrids are related to the corresponding unprimed hybrids by the two-fold axis.

The hybrid orbitals are the same as those used in Ueberhardt, Crawford and Lipscomb, however the directions of the hybrids on atoms 1 and 3 have been altered slightly to make them more nearly orthogonal to each other.



**Figure 3. Framework Hybrid Orbitals**

#### IV Group Theory and Overlap Integrals

Crystallographic data<sup>7</sup> show  $B_{10}H_{14}$  to have  $C_2$  symmetry although the symmetry is so close to  $C_{2v}$  that it is convenient to use this point group in developing the MO's. The character table<sup>8</sup> for  $C_{2v}$  is:

| $C_{2v}$ | E | $C_2$ | $\sigma_x$ | $\sigma_y$ |
|----------|---|-------|------------|------------|
| $A_1$    | 1 | 1     | 1          | 1          |
| $A_2$    | 1 | 1     | -1         | -1         |
| $B_1$    | 1 | -1    | 1          | -1         |
| $B_2$    | 1 | -1    | -1         | 1          |

The components of this matrix are  $X_i(R)$ .

The results of the application of the four symmetry operations of  $C_{2v}$  to the hybrid orbitals are:



|     | E          | C <sub>2</sub> | $\sigma_x$ | $\sigma_y$ |      |
|-----|------------|----------------|------------|------------|------|
| 1   | <u>1</u>   | 1'             | 1'         | <u>1</u>   |      |
| 2   | <u>2</u>   | 2'             | 2'         | <u>2</u>   |      |
| 3   | <u>3</u>   | 3'             | 3'         | <u>3</u>   |      |
| 4   | <u>4</u>   | 4'             | -4'        | <u>-4</u>  |      |
| 5   | <u>5</u>   | 5'             | 7'         | 7          |      |
| 6   | <u>6</u>   | 6'             | 8'         | 8          |      |
| 7   | <u>7</u>   | 7'             | 5'         | 5          |      |
| 8   | <u>8</u>   | 8'             | 6'         | 6          |      |
| 9   | <u>9</u>   | 9'             | <u>2</u>   | 9'         |      |
| 10  | <u>10</u>  | 10'            | 11         | 11'        |      |
| 11  | <u>11</u>  | 11'            | 10         | 10'        |      |
| 1'  | <u>1'</u>  | 1              | 1          | <u>1'</u>  |      |
| 2'  | <u>2'</u>  | 2              | 2          | <u>2'</u>  |      |
| 3'  | <u>3'</u>  | 3              | 3          | <u>3'</u>  |      |
| 4'  | <u>4'</u>  | 4              | -4         | <u>-4'</u> |      |
| 5'  | <u>5'</u>  | 5              | 7          | 7'         |      |
| 6'  | <u>6'</u>  | 6              | 8          | 8'         |      |
| 7'  | <u>7'</u>  | 7              | 5          | 5'         |      |
| 8'  | <u>8'</u>  | 8              | 6          | 6'         |      |
| 9'  | <u>9'</u>  | 9              | <u>2'</u>  | 9          |      |
| 10' | <u>10'</u> | 10             | 11'        | 11         |      |
| 11' | <u>11'</u> | 11             | 10'        | 10         |      |
|     | 22         | 0              | 2          | 4          | X(R) |

The number of times an orbital transforms into itself under a given symmetry operation is  $X(R) = 22, 0, 2$  or  $4$ . The number of symmetry orbitals in each representation is

$$a_i = \frac{1}{h} \sum_R X(R) X_i(R)$$

or

$$a(a_1) = \frac{1}{4} [22 \cdot 1 + 0 \cdot 1 + 2 \cdot 1 + 4 \cdot 1] = 7$$

$$a(a_2) = \frac{1}{4} [22 \cdot 1 + 0 \cdot 1 - 2 \cdot 1 - 4 \cdot 1] = 4$$

$$a(b_1) = \frac{1}{4} [22 \cdot 1 - 0 \cdot 1 + 2 \cdot 1 - 4 \cdot 1] = 5$$

$$a(b_2) = \frac{1}{4} [22 \cdot 1 - 0 \cdot 1 - 2 \cdot 1 + 4 \cdot 1] = 6$$

The symmetry orbitals are then given by

$$\sum_R X_i(R) Rf$$

where  $Rf$  is the result of operation  $R$  on hybrid orbital  $f$ .

| $a_1$         | $a_2$         | $b_1$         | $b_2$         |
|---------------|---------------|---------------|---------------|
| 1+1'          | 0             | 0             | 1-1'          |
| 2+2'          | 0             | 0             | 2-2'          |
| 3+3'          | 0             | 0             | 3-3'          |
| 0             | 4+4'          | 4-4'          | 0             |
| 5+5'+7+7'     | 5+5'-7-7'     | 5-5'-7+7'     | 5-5'+7-7'     |
| 6+6'+8+8'     | 6+6'-8-8'     | 6-6'-8+8'     | 6-6'+8-8'     |
| 9+9'          | 0             | 9-9'          | 0             |
| 10+10'+11+11' | 10+10'-11-11' | 10-10'+11-11' | 10-10'-11+11' |

or

$$\begin{aligned}
 \phi_1 &= N_1 (1+1') & \phi_{12} &= N_{12}(4-4') \\
 \phi_2 &= N_2 (2+2') & \phi_{13} &= N_{13}(5-5'-7+7') \\
 \phi_3 &= N_3 (3+3') & \phi_{14} &= N_{14}(6-6'-8+8') \\
 \phi_4 &= N_4 (5+5'+7+7') & \phi_{15} &= N_{15}(9-9') \\
 \phi_5 &= N_5 (6+6'+8+8') & \phi_{16} &= N_{16}(10-10'+11-11') \\
 \phi_6 &= N_6 (9+9') & & \\
 \phi_7 &= N_7 (10+10'+11+11') & \phi_{17} &= N_{17}(1-1') \\
 & & \phi_{18} &= N_{18}(2-2') \\
 \phi_8 &= N_8 (4+4') & \phi_{19} &= N_{19}(3-3') \\
 \phi_9 &= N_9 (5+5'-7-7') & \phi_{20} &= N_{20}(5-5'+7-7') \\
 \phi_{10} &= N_{10} (6+6'-8-8') & \phi_{21} &= N_{21}(6-6'+8-8') \\
 \phi_{11} &= N_{11} (10+10'-11-11') & \phi_{22} &= N_{22}(10-10'-11+11')
 \end{aligned}$$

where  $N_i$  is the normalization factor. The  $N_i$ 's may be determined from

$$S_{nn} = 1 = \int \phi_n \phi_n d\tau.$$

In this paper all the  $\phi$ 's are real so the complex notation will be omitted.

All the hybrid orbital overlap integrals were evaluated and are listed in the appendix.<sup>9</sup> These integrals are necessary for calculating the  $N_i$ 's and the symmetry orbital overlap integrals:

$$S_{nm} = \int \phi_n \phi_m d\tau.$$

The  $N_i$ 's are listed in Table 3 and the symmetry orbital overlap integral values are listed in Table 4.

|          |         |          |         |
|----------|---------|----------|---------|
| $N_1$    | = 0.697 | $N_{12}$ | = 0.696 |
| $N_2$    | = 0.695 | $N_{13}$ | = 0.522 |
| $N_3$    | = 0.642 | $N_{14}$ | = 0.424 |
| $N_4$    | = 0.416 | $N_{15}$ | = 0.780 |
| $N_5$    | = 0.383 | $N_{16}$ | = 0.800 |
| $N_6$    | = 0.651 |          |         |
| $N_7$    | = 0.394 | $N_{17}$ | = 0.718 |
|          |         | $N_{18}$ | = 0.719 |
| $N_8$    | = 0.719 | $N_{19}$ | = 0.798 |
| $N_9$    | = 0.622 | $N_{20}$ | = 0.503 |
| $N_{10}$ | = 0.765 | $N_{21}$ | = 0.725 |
| $N_{11}$ | = 0.605 | $N_{22}$ | = 0.436 |

Table 3. Normalization Factors

$S_{12} = 0.744$   
 $S_{13} = .225$   
 $S_{14} = .593$   
 $S_{15} = .284$   
 $S_{16} = .256$   
 $S_{17} = .216$   
 $S_{23} = .054$   
 $S_{24} = .652$   
 $S_{25} = .272$   
 $S_{26} = .393$   
 $S_{27} = .172$   
 $S_{34} = .507$   
 $S_{35} = .485$   
 $S_{36} = .408$   
 $S_{37} = .795$   
 $S_{45} = .216$   
 $S_{46} = .479$   
 $S_{47} = .424$   
 $S_{56} = .703$   
 $S_{57} = .368$   
 $S_{67} = .087$

118

$S_8 9 = .642$   
 $S_8 10 = .132$   
 $S_8 11 = -.614$   
 $S_9 10 = -.394$   
 $S_9 11 = -.473$   
 $S_{10} 11 = -.254$   
  
 $S_{12} 13 = .568$   
 $S_{12} 14 = .286$   
 $S_{12} 15 = -.376$   
 $S_{12} 16 = -.278$   
 $S_{13} 14 = -.004$   
 $S_{13} 15 = -.433$   
 $S_{13} 16 = -.187$   
 $S_{14} 15 = -.710$   
 $S_{14} 16 = -.137$   
 $S_{15} 16 = -.212$   
  
 $S_{17} 18 = .725$   
 $S_{17} 19 = .152$   
 $S_{17} 20 = .632$   
 $S_{17} 21 = .175$   
 $S_{17} 22 = .234$   
 $S_{18} 19 = -.069$   
 $S_{18} 20 = .677$   
 $S_{18} 21 = .090$   
 $S_{18} 22 = .137$   
 $S_{19} 20 = .474$   
 $S_{19} 21 = .368$   
 $S_{19} 22 = .701$   
 $S_{20} 21 = -.185$   
 $S_{20} 22 = .526$   
 $S_{21} 22 = .330$

$$S_{nm} = \int \phi_n \phi_m d\tau$$

Table 4. Symmetry Orbital Overlap Integrals

# V LCAO-MO Treatment

The wave functions<sup>10</sup>

$$\psi_i = \sum_n C_{ni} \phi_n$$

$$\psi_{a_1} = C_1 \phi_1 + C_2 \phi_2 + C_3 \phi_3 + C_4 \phi_4 + C_5 \phi_5 + C_6 \phi_6 + C_7 \phi_7$$

$$\psi_{a_2} = C_8 \phi_8 + C_9 \phi_9 + C_{10} \phi_{10} + C_{11} \phi_{11}$$

$$\psi_{b_1} = C_{12} \phi_{12} + C_{13} \phi_{13} + C_{14} \phi_{14} + C_{15} \phi_{15} + C_{16} \phi_{16}$$

$$\psi_{b_2} = C_{17} \phi_{17} + C_{18} \phi_{18} + C_{19} \phi_{19} + C_{20} \phi_{20} + C_{21} \phi_{21} + C_{22} \phi_{22}$$

in the simple MO approximation lead to four sets of secular equations, that is one set of secular equations for each representation:

$$(\alpha_n - E)C_n + \sum'_m (\beta_{nm} - S_{nm}E)C_m = 0, \text{ for } n = 1, 2 \dots, m \neq n$$

where  $\alpha_n = \int \phi_n^* H \phi_n d\tau,$

$$\beta_{nm} = \int \phi_n^* H \phi_m d\tau,$$

and H is the effective one-electron Hamiltonian. It must be remembered that the  $\phi_n$ 's are symmetry orbitals and must be written out in terms of individual atomic orbitals in order to evaluate  $\alpha_n$ . Assuming  $\beta_{nm} = KS_{nm}$ , the secular equations become

$$(\alpha_n - E)C_n + \sum'_m (K - E) S_{nm} C_m = 0. \quad \text{I}$$

If it is then assumed that  $\alpha_n = \alpha$ :

$$-X C_n + \sum'_m S_{nm} C_m = 0 \quad \text{II}$$

where  $-X = \frac{\alpha-E}{K-E}$  and  $E = \frac{\alpha+KX}{1+X}$

For both equations I and II there are 7 equations in  $a_1$ , 4 in  $a_2$ , 5 in  $b_1$  and 6 in  $b_2$ .

Two calculations were carried out, one using values of  $\alpha_n$  calculated from a simple charge distribution in decaborane (Calculation A) and one using values of  $\alpha_n$  calculated from valence state ionization energies of boron atomic orbitals (Calculation B). All solutions were carried out on the IBM 704 computer. A summary of the results of Calculation A appears in J. Chem. Phys., 35, 1329 (1961), E. B. Moore, Jr., L. L. Lohr, Jr., and W. N. Lipscomb.

## VI Calculation A

After all the overlap integrals  $S_{nm}$  were evaluated, equations II were solved. The resulting charge distribution was then used to approximate values of  $\alpha_n$  from a formula for atomic orbital Coulomb integrals suggested by Moffit and modified for the iron hydrides by Abernethy, Crawford and Lipscomb<sup>4</sup>:

$$\xi_j^i = -I + (I-E) (W_j^i - 2)$$

where  $W_j^i$  represents the total electron density on atom  $j$ , less one electron in the molecular orbital  $\psi_i$  for which the calculation is being made, and  $I$  and  $E$  are the valence state ionization potential and electron affinity.

With these values of  $\alpha_n$  and several different values of  $K$ , equations I were solved on the IBM 704. A value of  $K = -21$  gave the best results. The secular equations are listed in Table 5 and the energies and MO coefficients for all 22 MO's are listed in Table 6. The coefficients are normalized according to

$$\int \psi_i \psi_i d\tau = 1 .$$

The eight wave functions (bonding) of lowest energy are listed in Table 7.



$$\begin{aligned}
& \left( \frac{-4.885-E}{-21-E} \right) c_1 + (.744) c_2 + (.225) c_3 + (.593) c_4 + (.284) c_5 + (.256) c_6 + (.216) c_7 = 0 \\
& + \left( \frac{-1.272-E}{-21-E} \right) c_2 + (.054) c_3 + (.652) c_4 + (.272) c_5 + (.393) c_6 + (.172) c_7 = 0 \\
& + \left( \frac{-4.200-E}{-21-E} \right) c_3 + (.507) c_4 + (.485) c_5 + (.408) c_6 + (.795) c_7 = 0 \\
& + \left( \frac{-7.847-E}{-21-E} \right) c_4 + (.216) c_5 + (.479) c_6 + (.424) c_7 = 0 \\
& + \left( \frac{-2.849-E}{-21-E} \right) c_5 + (.703) c_6 + (.368) c_7 = 0 \\
& + \left( \frac{-2.200-E}{-21-E} \right) c_6 + (.087) c_7 = 0 \\
& + \left( \frac{-7.219-E}{-21-E} \right) c_7 = 0
\end{aligned}$$

$a_1$

$$\begin{aligned}
& \left( \frac{+1.994-E}{-21-E} \right) c_8 + (.642) c_9 + (.132) c_{10} + (-.614) c_{11} = 0 \\
& + \left( \frac{+5.743-E}{-21-E} \right) c_9 + (-.394) c_{10} + (-.473) c_{11} = 0 \\
& + \left( \frac{+19.451-E}{-21-E} \right) c_{10} + (-.254) c_{11} = 0 \\
& + \left( \frac{+11.697-E}{-21-E} \right) c_{11} = 0
\end{aligned}$$

$a_2$

Table 5. Calculation A Secular Equations (symmetric about the diagonal)

$$\begin{aligned}
& \left( \frac{+0.860-E}{-21-E} \right) c_{12} + (.568) c_{13} + (.286) c_{14} + (-.376) c_{15} + (-.278) c_{16} = 0 \\
& + \left( \frac{-0.514-E}{-21-E} \right) c_{13} + (-.004) c_{14} + (-.433) c_{15} + (-.187) c_{16} = 0 \\
& + \left( \frac{-7.511-E}{-21-E} \right) c_{14} + (-.710) c_{15} + (-.137) c_{16} = 0 \\
b_1 & + \left( \frac{+2.054-E}{-21-E} \right) c_{15} + (-.212) c_{16} = 0 \\
& + \left( \frac{+27.438-E}{-21-E} \right) c_{16} = 0
\end{aligned}$$

$$\begin{aligned}
& \left( \frac{-3.764-E}{-21-E} \right) c_{17} + (.725) c_{18} + (.152) c_{19} + (.632) c_{20} + (.175) c_{21} + (.234) c_{22} = 0 \\
& + \left( \frac{+0.096-E}{-21-E} \right) c_{18} + (-.069) c_{19} + (.677) c_{20} + (.090) c_{21} + (.137) c_{22} = 0 \\
& + \left( \frac{+4.934-E}{-21-E} \right) c_{19} + (.474) c_{20} + (.368) c_{21} + (.701) c_{22} = 0 \\
b_2 & + \left( \frac{-2.017-E}{-21-E} \right) c_{20} + (-.185) c_{21} + (.526) c_{22} = 0 \\
& + \left( \frac{+18.553-E}{-21-E} \right) c_{21} + (.330) c_{22} = 0 \\
& + \left( \frac{-3.899-E}{-21-E} \right) c_{22} = 0
\end{aligned}$$

Table 5. (continued)

|                | (1)       | (2)      | (3)      | (4)      | (5)      | (6)       | (7)       |
|----------------|-----------|----------|----------|----------|----------|-----------|-----------|
| $E(\text{ev})$ | -16.5929  | -10.4173 | -8.17019 | 6.42541  | 36.8305  | 112.261   | 298.898   |
| $c_1$          | .177014   | .381746  | -.042139 | -.632698 | 1.124129 | .172353   | -1.181639 |
| $c_2$          | .140598   | .355433  | .039612  | -.217838 | -.938799 | 1.013727  | 1.739796  |
| $c_3$          | .195121   | -.312454 | -.237695 | .231826  | .805514  | .909197   | 2.391154  |
| $c_4$          | .262843   | .303433  | -.269276 | .761763  | -.127073 | -1.809197 | .000985   |
| $c_5$          | .280602   | -.340120 | .636292  | -.514806 | -.188229 | -1.491882 | .866246   |
| $c_6$          | .159711   | -.017293 | .392271  | .585222  | .021177  | 1.252100  | -1.886190 |
| $c_7$          | .209751   | -.340225 | -.501053 | -.391192 | -.788258 | .304240   | -2.194618 |
| $E(\text{ev})$ | -8.70204  | 6.76813  | 55.5297  | 151.592  |          |           |           |
| $c_8$          | .490124   | .196930  | 1.132978 | -.999345 |          |           |           |
| $c_9$          | .387060   | -.488223 | -.151560 | 1.678644 |          |           |           |
| $c_{10}$       | -.006083  | .653200  | .187964  | 1.238765 |          |           |           |
| $c_{11}$       | -.290867  | -.314917 | 1.172759 | .610753  |          |           |           |
| $E(\text{ev})$ | -12.46571 | -5.72007 | 11.8579  | 38.9409  | 314.741  |           |           |
| $c_{12}$       | .254524   | .377992  | .518084  | 1.108981 | -.198871 |           |           |
| $c_{13}$       | .205800   | .591866  | -.345785 | -.778762 | 1.551369 |           |           |
| $c_{14}$       | .528597   | -.587352 | .354896  | -.301114 | 2.126671 |           |           |
| $c_{15}$       | -.326223  | .065225  | .610001  | .000294  | 2.545774 |           |           |
| $c_{16}$       | -.024061  | -.068718 | -.542653 | .633014  | 1.245581 |           |           |

Table 6. Calculation A Orbital Energy Values and Normalized MO Coefficients

| $E(\text{ev})$ | (1)      | (2)      | (3)      | (4)      | (5)       | (6)       |
|----------------|----------|----------|----------|----------|-----------|-----------|
| $b_2$          |          |          |          |          |           |           |
| $C_{17}$       | -14.0339 | -7.72074 | 9.41392  | 39.7168  | 63.2461   | 2919.20   |
| $C_{18}$       | .322961  | -.322561 | .465767  | -.906062 | -1.096318 | -.922452  |
| $C_{19}$       | .241174  | -.361243 | .124660  | .828043  | .853177   | -5.081453 |
| $C_{20}$       | .144305  | .373398  | -.011758 | -.791841 | .818943   | -4.464396 |
| $C_{21}$       | .331873  | -.050237 | -.645506 | -.115016 | .462480   | 7.710808  |
| $C_{22}$       | .034131  | .115166  | .682655  | .132418  | .456629   | 4.210795  |
|                | .271912  | .515509  | -.008147 | .933333  | -1.039356 | -1.412111 |

Table 6. (continued)

| E(ev)   |  |
|---------|--|
| -16.593 | $\psi_{a_1}(1) = +.177\epsilon_1 + .141\epsilon_2 + .195\epsilon_3 + .263\epsilon_4 + .281\epsilon_5 + .160\epsilon_6 + .210\epsilon_7$  |
| -10.417 | $\psi_{a_1}(2) = +.382\epsilon_1 + .355\epsilon_2 - .312\epsilon_3 + .303\epsilon_4 - .340\epsilon_5 - .017\epsilon_6 - .340\epsilon_7$  |
| - 8.170 | $\psi_{a_1}(3) = -.042\epsilon_1 + .040\epsilon_2 - .238\epsilon_3 - .269\epsilon_4 + .636\epsilon_5 + .392\epsilon_6 - .501\epsilon_7$  |
| - 8.702 | $\psi_{a_2}(1) = .140\epsilon_8 + .387\epsilon_9 - .006\epsilon_{10} - .291\epsilon_{11}$  |
| -12.466 | $\psi_{b_1}(1) = .255\epsilon_{12} + .206\epsilon_{13} + .529\epsilon_{14} - .326\epsilon_{15} - .024\epsilon_{16}$                      |
| - 5.720 | $\psi_{b_1}(2) = .378\epsilon_{12} + .592\epsilon_{13} - .587\epsilon_{14} + .065\epsilon_{15} - .069\epsilon_{16}$                      |
| -14.034 | $\psi_{b_2}(1) = +.323\epsilon_{17} + .241\epsilon_{18} + .144\epsilon_{19} + .332\epsilon_{20} + .034\epsilon_{21} + .272\epsilon_{22}$ |
| - 7.721 | $\psi_{b_2}(2) = -.323\epsilon_{17} - .361\epsilon_{18} + .373\epsilon_{19} - .050\epsilon_{20} + .115\epsilon_{21} + .516\epsilon_{22}$ |

Table 7. Calculation A Bonding Wave Functions and Energies

## VII Calculation B

For purposes of comparison and also to make the results more reproducible, it was decided to repeat the calculation using more easily derived values of  $\alpha_n$  based on valence state ionization potentials of boron atomic orbitals. The  $\alpha_n$ 's were written out in terms of Coulomb integrals involving pure s and pure p orbitals only. The  $\alpha_n$ 's were then evaluated using the values for boron s and p Coulomb integrals suggested by Mulliken<sup>11</sup>:

$$\int \phi_{B2s}^2 H \phi_{B2s}^2 d\tau = -15.36\text{ev} \quad \int \phi_{B2p}^2 H \phi_{B2p}^2 d\tau = -8.63\text{ev}.$$

Equations I were solved three different times using  $K = -25, -21$  and  $-15$  ev. The resulting charge distributions were nearly the same in all three cases but  $K = -15$  gave the best dipole moment and ionization potential. The results indicate that  $K = -12$  might have given a slightly better dipole moment and ionization potential without affecting the charge distribution appreciably. The secular equations are given in Table 8, the orbital energy values and MO coefficients for all 22 MO's are listed in Table 9 and the bonding MO's and corresponding orbital energies are given in Table 10.

$$\begin{aligned}
& \left( \frac{-10.462-E}{-15-E} \right) c_1 + (.744) c_2 + (.225) c_3 + (.593) c_4 + (.284) c_5 + (.256) c_6 + (.216) c_7 = 0 \\
& \left( \frac{-10.996-E}{-15-E} \right) c_2 + (.054) c_3 + (.652) c_4 + (.272) c_5 + (.393) c_6 + (.172) c_7 = 0 \\
& \left( \frac{-11.604-E}{-15-E} \right) c_3 + (.507) c_4 + (.485) c_5 + (.408) c_6 + (.795) c_7 = 0 \\
& \left( \frac{-11.766-E}{-15-E} \right) c_4 + (.216) c_5 + (.479) c_6 + (.424) c_7 = 0 \\
& \left( \frac{-12.261-E}{-15-E} \right) c_5 + (.703) c_6 + (.368) c_7 = 0 \\
& \left( \frac{-11.022-E}{-15-E} \right) c_6 + (.087) c_7 = 0 \\
& \left( \frac{-12.077-E}{-15-E} \right) c_7 = 0 \\
\\
& \left( \frac{-8.412-E}{-15-E} \right) c_8 + (.642) c_9 + (.132) c_{10} + (-.614) c_{11} = 0 \\
& \left( \frac{-7.745-E}{-15-E} \right) c_9 + (-.394) c_{10} + (-.473) c_{11} = 0 \\
& \left( \frac{-4.022-E}{-15-E} \right) c_{10} + (-.254) c_{11} = 0 \\
& \left( \frac{-8.137-E}{-15-E} \right) c_{11} = 0
\end{aligned}$$

Table 8. Calculation B Secular Equations (symmetric about the diagonal)

$$\left(\frac{-8.842-E}{-15-E}\right) c_{12} + (.568) c_{13} + (.286) c_{14} + (-.376) c_{15} + (-.278) c_{16} = 0$$

$$\left(\frac{-9.900-E}{-15-E}\right) c_{13} + (-.004) c_{14} + (-.433) c_{15} + (-.187) c_{16} = 0$$

$$\left(\frac{-11.654-E}{-15-E}\right) c_{14} + (-.710) c_{15} + (-.137) c_{16} = 0$$

$$b_1 \quad \left(\frac{-9.263-E}{-15-E}\right) c_{15} + (-.212) c_{16} = 0$$

$$\left(\frac{-3.016-E}{-15-E}\right) c_{16} = 0$$

$$\left(\frac{-10.169-E}{-15-E}\right) c_{17} + (.725) c_{18} + (.152) c_{19} + (.632) c_{20} + (.175) c_{21} + (.234) c_{22} = 0$$

$$\left(\frac{-10.715-E}{-15-E}\right) c_{18} + (-.069) c_{19} + (.677) c_{20} + (.090) c_{21} + (.137) c_{22} = 0$$

$$\left(\frac{-9.763-E}{-15-E}\right) c_{19} + (.474) c_{20} + (.360) c_{21} + (.701) c_{22} = 0$$

$$b_2 \quad \left(\frac{-10.285-E}{-15-E}\right) c_{20} + (-.185) c_{21} + (.526) c_{22} = 0$$

$$\left(\frac{-5.127-E}{-15-E}\right) c_{21} + (.330) c_{22} = 0$$

$$\left(\frac{-11.452-E}{-15-E}\right) c_{22} = 0$$

Table 8. (continued)



|                | (1)        | (2)        | (3)        | (4)       | (5)       | (6)      | (7)      |
|----------------|------------|------------|------------|-----------|-----------|----------|----------|
| $E(\text{ev})$ | -13.994455 | -12.621354 | -12.074236 | -8.507018 | -1.486525 | 15.2206  | 53.272   |
| $c_1$          | .135278    | .289890    | .139879    | .479038   | -1.17226  | .166157  | -1.23110 |
| $c_2$          | .150523    | .414475    | .098263    | .329770   | .859285   | 1.05562  | 1.72205  |
| $c_3$          | .229162    | -.371780   | .126732    | -.334349  | -.802687  | 1.01200  | 2.33496  |
| $c_4$          | .240575    | .245305    | .315145    | -.722144  | .146032   | -1.82692 | .074042  |
| $c_5$          | .260960    | -.137711   | -.664256   | .599085   | .069906   | -1.45886 | .924931  |
| $c_6$          | .171361    | .101550    | -.430154   | -.592512  | .140795   | 1.16571  | -1.92188 |
| $c_7$          | .236131    | -.434754   | .404377    | .441761   | .821305   | .208200  | -2.18467 |
| $E(\text{ev})$ | -11.811800 | -7.7046    | 3.4440     | 31.550718 |           |          |          |
| $c_8$          | .436309    | .101134    | 1.10469    | -1.03787  |           |          |          |
| $c_9$          | .359319    | -.514853   | -.057506   | 1.63271   |           |          |          |
| $c_{10}$       | .005249    | .623685    | .314139    | 1.23837   |           |          |          |
| $c_{11}$       | -.381071   | -.380278   | 1.16396    | .530462   |           |          |          |
| $E(\text{ev})$ | -12.841735 | -11.107273 | -6.680964  | 0.808198  | 68.296681 |          |          |
| $c_{12}$       | .217417    | .344032    | .463974    | 1.15036   | -203059   |          |          |
| $c_{13}$       | .198789    | .628920    | -.277867   | -.773990  | 1.55375   |          |          |
| $c_{14}$       | .550578    | -.568831   | .364912    | -.279752  | 2.12736   |          |          |
| $c_{15}$       | -.335979   | .035780    | .607769    | .041108   | 2.54530   |          |          |
| $c_{16}$       | -.022365   | -.068752   | -.580783   | .601263   | 1.24415   |          |          |

Table 9. Calculation B Orbital Energy Values and Normalized MO Coefficients

| b <sub>2</sub>  | E(ev) | -13.381023 | -12.144603 | -7.345380 | -1.7469  | 4.573038 | 666.678  |
|-----------------|-------|------------|------------|-----------|----------|----------|----------|
|                 |       |            |            |           |          |          |          |
| C <sub>17</sub> |       | .249124    | -.279218   | .392308   | .679715  | -1.29064 | .936657  |
| C <sub>18</sub> |       | .258198    | -.437497   | .194782   | -.587094 | 1.05170  | 5.06862  |
| C <sub>19</sub> |       | .184910    | .372332    | -.025000  | .947712  | .689789  | 4.45426  |
| C <sub>20</sub> |       | .307722    | -.095239   | -.645131  | .188415  | .343677  | -7.71598 |
| C <sub>21</sub> |       | .036873    | .091092    | .695950   | -.005074 | .400070  | -4.21691 |
| C <sub>22</sub> |       | .333457    | .477128    | .016246   | -1.14763 | -.779760 | 1.42157  |

Table 9. (continued)

E(ev)

|          |  |
|----------|--|
| -13.9945 | $\psi_{a_1}(1) = .1353\epsilon_1 + .1505\epsilon_2 + .2292\epsilon_3 + .2406\epsilon_4 + .2610\epsilon_5 + .1714\epsilon_6 + .2361\epsilon_7$  |
| -12.6214 | $\psi_{a_1}(2) = .2899\epsilon_1 + .4145\epsilon_2 - .3718\epsilon_3 + .2453\epsilon_4 - .1377\epsilon_5 + .1016\epsilon_6 - .4348\epsilon_7$  |
| -12.0742 | $\psi_{a_1}(3) = .1399\epsilon_1 + .0983\epsilon_2 + .1267\epsilon_3 + .3151\epsilon_4 - .6643\epsilon_5 - .4302\epsilon_6 + .4044\epsilon_7$  |
| -11.8118 | $\psi_{a_2}(1) = .4364\epsilon_8 + .3593\epsilon_9 + .0052\epsilon_{10} - .3811\epsilon_{11}$  |
| -12.8417 | $\psi_{b_1}(1) = .2174\epsilon_{12} + .1938\epsilon_{13} + .5506\epsilon_{14} - .3360\epsilon_{15} - .0224\epsilon_{16}$                       |
| -11.1073 | $\psi_{b_1}(2) = .3440\epsilon_{12} + .6289\epsilon_{13} - .5688\epsilon_{14} + .0358\epsilon_{15} - .0688\epsilon_{16}$                       |
| -13.3810 | $\psi_{b_2}(1) = .2491\epsilon_{17} + .2582\epsilon_{18} + .1849\epsilon_{19} + .3077\epsilon_{20} + .0369\epsilon_{21} + .3335\epsilon_{22}$  |
| -12.1446 | $\psi_{b_2}(2) = -.2792\epsilon_{17} - .4375\epsilon_{18} + .3724\epsilon_{19} - .0952\epsilon_{20} + .0911\epsilon_{21} + .4771\epsilon_{22}$ |

" : 10. Calculation B Bonding Wave Functions

### VIII Population Analysis and Charge Distribution

A population analysis<sup>2</sup>, carried out using the eight MO's of lowest energy (Tables 7 and 10), yields negative charges associated with each symmetry orbital as shown in Table 11. If the MO's are written as

$$\psi_i = \sum_n C_{ni} \phi_n,$$

and each MO  $\psi_i$  is assumed to be doubly occupied, the population matrix is given by

$$[q_{nm}] = 2S_{nm} \sum_i C_{ni} C_{mi}.$$

The gross atomic population, or sum of each column or row of the matrix

$$\sum_n q_{nm},$$

is a measure of the negative charge associated with each symmetry orbital. These charges may then be rearranged to show the negative charge associated with each boron atom and, when account is taken of the positive charge on each boron, to show the net formal charge associated with each boron. The net charge is listed in Table 12, and shown schematically in Figure 4 for Calculation B. The fractions are the charges resulting from the three-center bond treatment.

|             | A       | B      |
|-------------|---------|--------|
| $\phi_1$    | -0.677e | -.547e |
| $\phi_2$    | .652    | .785   |
| $\phi_3$    | .749    | .783   |
| $\phi_4$    | .790    | .752   |
| $\phi_5$    | 1.346   | 1.242  |
| $\phi_6$    | .670    | .771   |
| $\phi_7$    | 1.118   | 1.117  |
| $\phi_8$    | .898    | .787   |
| $\phi_9$    | .653    | .588   |
| $\phi_{10}$ | .000    | .001   |
| $\phi_{11}$ | .450    | .625   |
| $\phi_{12}$ | .741    | .645   |
| $\phi_{13}$ | 1.143   | 1.223  |
| $\phi_{14}$ | 1.492   | 1.497  |
| $\phi_{15}$ | .588    | .602   |
| $\phi_{16}$ | .037    | .035   |
| $\phi_{17}$ | .787    | .633   |
| $\phi_{18}$ | .767    | .927   |
| $\phi_{19}$ | .701    | .730   |
| $\phi_{20}$ | .606    | .580   |
| $\phi_{21}$ | .092    | .074   |
| $\phi_{22}$ | 1.045   | 1.054  |

Table 11. Negative Charge Associated with Each Symmetry Orbital.

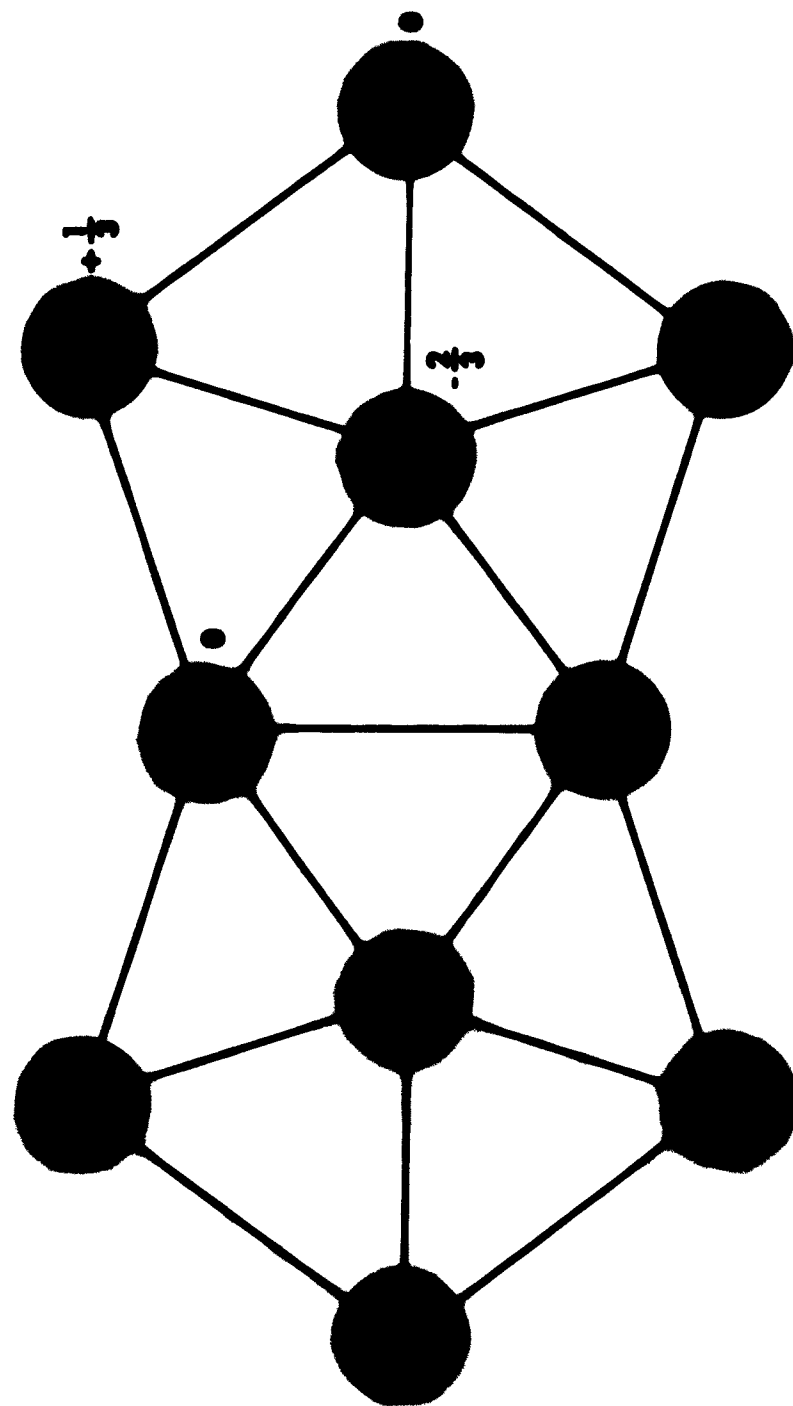
### Calculation A

| Atoms    | Total<br>Negative<br>Charge | Total<br>Positive<br>Charge | Total<br>Net<br>Charge | Net Charge<br>Per Atom |
|----------|-----------------------------|-----------------------------|------------------------|------------------------|
| 1,3      | -3.908e                     | +4e                         | +.092e                 | +.046e                 |
| 2,4      | -4.508                      | +4                          | -.508                  | -.254                  |
| 6,9      | -1.464                      | +2                          | +.536                  | +.268                  |
| 5,7,8,10 | -6.122                      | +6                          | -.122                  | -.031                  |

### Calculation B

|          |         |     |        |        |
|----------|---------|-----|--------|--------|
| 1,3      | -4.204e | +4e | -.204e | -.102e |
| 2,4      | -4.657  | +4  | -.657  | -.329  |
| 6,9      | -1.180  | +2  | +.820  | +.410  |
| 5,7,8,10 | -5.957  | +6  | +.043  | +.011  |

Table 12. Formal Charge Distribution



**Figure 4. Calculation B Charge Distribution  
(bridge hydrogens not included)**

## IX Dipole Moment

Table 13 gives the observed dipole moment, the three-center bond dipole moment (ECL) and the LCAO-MO framework dipole moment.

|                   |        |
|-------------------|--------|
| Observed          | 3.52 D |
| Three-center Bond | 6.1    |
| Calculation A     | 3.6    |
| Calculation B     | 7.3    |

Table 13. Dipole Moment



## X Discussion

The structure<sup>12</sup> of the electrophilic substitution compound  $B_{10}H_{12}I_2$ , which results from the direct attack of iodine on decaborane indicates that boron atoms 2 and 4 are the most negative. Similarly the structure<sup>13</sup> of  $B_{10}H_{12}(CH_3CN)_2$  indicates that atoms 6 and 9 are the most positive, that is, the most susceptible to substitutional attack by an electron donor. The structure of each of these compounds has been determined by means of X-ray diffraction. The interpretation of experimental evidence concerning the charges on atoms 1, 3 and 5, 7, 8, 10 is not yet entirely clear<sup>14,15,16,17</sup> but recent results concerning Friedel-Crafts alkylation<sup>18,19</sup> of decaborane and nucleophilic substitution<sup>20</sup> in decaborane suggest<sup>19,20</sup> that the order of charge excess is

$$(\text{neg}) 2, 4 < 1, 3 < 5, 7, 8, 10 < 6, 9 (\text{pos}).$$

The charge distribution of Calculation B is in agreement with the experimental charge order.

Since theory and experiment indicate that the bridge hydrogens in  $B_2H_6$  are .2e negatively charged, it is possible that the bridge hydrogens in  $B_{10}H_{14}$  are also negatively charged. With this modification, the charge distribution for Calculation B becomes:

| 2,4     | 1,3     | 5,7,8,10 | 6,9     | Bridge<br>H |
|---------|---------|----------|---------|-------------|
| -0.329e | -0.102e | +0.111e  | +0.610e | -0.2e       |

No account was taken of the bridge hydrogen asymmetry. This asymmetry would make 5,7,8 and 10 more positive. With this charge distribution, which also agrees with the experimental charge distribution, the dipole moment for Calculation B becomes 3.8 D, in reasonable agreement with the observed dipole moment. The calculated dipole moment would be increased by

breakdown of the charge into individual orbital contributions and decreased by electron-electron repulsions.

Pimentel and Pitzer<sup>21</sup> and Haaland<sup>22</sup> have measured the electronic spectrum of decaborane. Haaland found that the first transition is polarized in the x or y direction. This is predicted by both Calculation A and Calculation B:

$$\Psi_{b_1}(2) \rightarrow \Psi_{a_1}(4) \quad B_1 \quad x \quad \text{or}$$

$$\Psi_{b_1}(2) \rightarrow \Psi_{a_2}(2) \quad B_2 \quad y$$

where  $B_1$  and  $B_2$  refer to the symmetry of the complete wave function of the excited state.  $A_1$  is the symmetry of the complete wave function of the ground state and both transitions are allowed<sup>23</sup>.

If the bonding MO's are superimposed on Figure 3 large bonding, i.e. nodeless, regions are evident. In five of the eight bonding MO's the electron pair is spread over all ten boron atoms. In the other three bonding MO's the electron pair is spread over eight boron atoms.

Finally it is to be noted that the absolute value of the highest bonding orbital energy for Calculation B, 11.1 ev, corresponds favorably to the observed ionization energy, 11.0 ev as reported by Margrave<sup>24</sup> and 10.3 ev as reported by Kaufman<sup>25</sup>.

In conclusion, a rather simple group theory and MO calculation has yielded eight bonding wave functions for the 16 framework electrons of decaborane-14. The delocalization shows the metal-like nature of the molecule. The highest bonding energy level, the charge distribution, the dipole moment and the first two allowed transitions have been shown to be in agreement with experimental evidence.

## XI Acknowledgement

The author wishes to acknowledge the interest, encouragement and help of Professor William N. Lipscomb. The author also wishes to acknowledge the use of the Boeing Company IBM 704 computer and the programming and computing help of Mr. Arnold Rom and Mr. Dale Speakes.

### XII References

1. W. N. Lipscomb, *Advances in Inorganic and Radiochemistry*, I, 117 (1959)
2. W. C. Hamilton, *Proc. Roy. Soc. (London)*, A235, 395 (1956)
3. R. A. Ogg, *J. Chem. Phys.* 22, 1933 (1954)
4. W. H. Eberhardt, B. L. Crawford and W. N. Lipscomb, *J. Chem. Phys.*, 22, 989 (1954)
5. A. W. Laubengayer and R. Bottei, *J. Am. Chem. Soc.*, 74, 1618, (1952)
6. E. B. Moore, Jr., R. E. Dickerson and W. N. Lipscomb, *J. Chem. Phys.*, 27, 209, (1957)
7. J. S. Kasper, C. M. Lucht and D. Harker, *Acta Cryst.*, 3, 436 (1950)
8. H. Eyring, J. Walter and G. Kimball, *Quantum Chemistry*, John Wiley and Sons, New York, 384, (1954)
9. E. B. Moore, Jr., "Overlap Integrals", Boeing Scientific Research Laboratories Document D1-82-0067, (1960)
10. H. C. Longuet-Higgins and M. deV. Roberts, *Proc. Roy. Soc. (London)*, A224, 336 (1954)
11. R. S. Mulliken, *J. Chem. Phys.*, 2, 782 (1934)
12. R. Schaeffer, *J. Am. Chem. Soc.*, 79, 2726 (1957)
13. J. Reddy and W. N. Lipscomb, *J. Chem. Phys.*, 31, 610 (1959)
14. R. Schaeffer, J. N. Shoolery and R. Jones, *J. Am. Chem. Soc.*, 80 2670 (1958)
15. J. A. Dupont and M. F. Hawthorne, *J. Am. Chem. Soc.*, 81, 4998 (1959)
16. J. A. Dupont and M. F. Hawthorne, *Abstracts of the 138th Meeting of the American Chemical Society*, Sept. 1960, P. 46N
17. M. Hillman, *J. Am. Chem. Soc.*, 82, 1096 (1960)
18. N. J. Blay, I. Dunstan and R. L. Williams, *J. Chem. Soc.*, 1960, 430
19. R. L. Williams, I. Dunstan and N. J. Blay, *J. Chem. Soc.*, 1960, 5006
20. I. Dunstan, R. L. Williams and N. J. Blay, *J. Chem. Soc.*, 1960, 5012
21. G. C. Pimentel and K. S. Pitzer, *J. Chem. Phys.*, 17, 882 (1949)
22. A. Haaland, Ph.D. Thesis, Georgia Institute of Technology, Atlanta, Georgia, August 1961

23. H. Sponer and E. Teller, Rev. Mod. Phys., 13, 75 (1941)
24. J. L. Margrave, J. Chem. Phys., 32, 1889 (1960)
25. J. J. Kaufman, private communication, 1961

## Appendix

### I New Structures

It should be pointed out that the structure of a new decaborane has recently been determined<sup>1</sup>. The new compound has the formula  $B_{10}H_{16}$ . Also the structures of several boron hydride ions have recently been reported<sup>2,3</sup>:  $B_3H_8^-$  and  $B_{12}H_{12}^{-2}$ . The structure<sup>4</sup> of the compound  $B_{10}H_{12}[S(CH_3)_2]_2$  is also known.

1. R. Grimes, F. E. Wang, R. Lewin and W. N. Lipscomb, Proc. Nat. Acad. Sci., 47, 996 (1961)
2. C. R. Peters and C. E. Nordman, J. Am. Chem. Soc., 82, 5758 (1960)
3. J. A. Munderlich and W. N. Lipscomb, J. Am. Chem. Soc., 82, 4427 (1960)
4. D. E. Sands and A. Zalkin, Acta Cryst., 13, 1030 (1960)

## II Hybrid Orbital Overlap Integrals

|   |                |               |               |
|---|----------------|---------------|---------------|
| S | 1 1' = 0.030   | *2 3 = .052   | 6 9 = .084    |
|   | 2 2' = .034    | 2 3' = .060   | 6 9' = .621   |
|   | 3 3' = .214    | 2 5 = .516    | 6 10 = .158   |
|   | 4 4' = -.033   | 2 5' = .048   | 6 10' = .078  |
|   | 5 5' = .046    | 2 6 = .149    | 6 11 = .096   |
|   | 6 6' = .066    | 2 6' = .106   | 6 11' = .277  |
|   | 9 9' = .179    | 2 9 = .217    | *9 10 = .120  |
|   | 10 10' = .146  | 2 10 = .133   | 9 10' = .085  |
|   | 5 7 = .218     | 2 11 = .024   | 4 5 = .375    |
|   | 5 7' = .182    | 3 5 = .385    | 4 5' = -.016  |
|   | 6 8 = .090     | 3 5' = .090   | 4 6 = .151    |
|   | 6 8' = .549    | 3 6 = .326    | 4 6' = -.091  |
|   | *10 11 = -.125 | 3 6' = .167   | 4 9' = .173   |
|   | 10 11' = .463  | 3 9 = .244    | 4 10 = -.239  |
|   | 1 2 = .735     | 3 10 = .645   | 4 10' = -.114 |
|   | 1 2' = .033    | 3 11 = .141   |               |
|   | 1 3 = .192     | *5 6 = .315   |               |
|   | 1 3' = .059    | 5 6' = .066   |               |
|   | 1 5 = .471     | 5 8 = .106    |               |
|   | 1 5' = .040    | 5 8' = .167   |               |
|   | 1 6 = .175     | 5 9 = .088    |               |
|   | 1 6' = .091    | 5 9' = .354   |               |
|   | 1 9 = .141     | 5 10 = .205   |               |
|   | 1 10 = .192    | 5 10' = -.039 |               |
|   | 1 11 = .005    | 5 11 = .062   |               |
|   |                | 5 11' = .418  |               |

The starred integrals do not calculate to zero as the hybrid orbital directions were chosen to fit the molecule rather than exact orthogonality. The value zero was used in the calculations, however. In the case of  $S_{5\ 6}$  the appreciable error in orthogonality enters the calculation mainly as a rather small error in  $S_{6\ 9}$ . The hybrid orbital overlap integrals are not to be confused with the symmetry orbital overlap integrals listed in Table 4.